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SYNERGISTIC INSECTICIDAL MIXTURES  
[Insektizide synergistische Gemische]

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## SYNERGISTIC INSECTICIDAL MIXTURES

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(Separated part of Patent Application Sch 29 672 IVa/45 1)

It was found that the efficacy of insecticidally effective 1-naphthyl-N-methyl carbamate is synergistically increased by the addition of insecticidally ineffective carbamates.

As defined by the present invention, insecticidally ineffective carbamates are compounds that, up to a dose of approximately 0.8 mg/dm<sup>2</sup>, have virtually no insecticidal effect, whereas 1-naphthyl-N-methyl carbamate is fully effective below this dose.

In contrast to the use of insecticidally effective carbamates alone in pest control, the use of the mixtures according to the present invention increases especially the degree of efficacy, as well as the initial effect, that means that insect control can be more specifically designed. In addition, it was found that by using mixtures rather than the insecticidally effective carbamate alone, it is possible to reduce the toxicity to warm-blooded animals, that means that when using these mixtures rather than the individual insecticidally effective components contained in these mixtures, it is possible for the control of injurious insects to be carried out more safely for the user, as well as for domestic animals and pets.

Compounds of the class of carbamates for that an insecticidal efficacy was established include, e.g.,

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3-methyl-5-isopropylphenyl-N-methyl carbamate,

1-naphthyl-N-methyl carbamate,

3-isopropylphenyl-N-methyl carbamate,

5-(1-isopropyl-3-methylpyrazolyl)-N,N-dimethyl carbamate.

It is also known that the use of the mixtures of 2 different carbamate insecticides known from the prior art leads to an increase in efficacy that is markedly higher than the additive effect expected, that is known as analog synergism. However, this observation is of no general importance, since predictions

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\* [Numbers in right margin indicate pagination of the original text.]

about the potentiating effect inherent in a compound after combining this compounds with known biologically active substances are not possible because of the currently still lacking insight into the mechanisms of action in the insect organism that underlie the synergism. It was therefore surprising to discover that according to the present invention, mixtures of insecticidally effective 1-naphthyl-N-methyl carbamate with ineffective carbamates develop a marked and, in all cases, significant synergism.

The synergistic mixtures according to the present invention can be used alone or in combination with other pest control agents, such as insecticides, acaricides or fungicides. The preparation takes place in a manner usually used for plant protection preparations, using liquid and solid carrier materials. Suitable liquid carrier materials are, among others, water, mineral oil or solvents; suitable solid carrier materials are, e.g., bentonite, bleaching clay, gypsum, lime, diatomaceous earth, pyrophyllite, silicon dioxide or talc. The preparations may also contain additives, e.g., emulsifying agents, wetting or binding agents, propellants, odoriferous substances, stabilizers, attractants or repellents. The preparations can be applied, for example, in the form of dust, spreading agents or granules, in form of misting, atomizable or sprayable liquids, or in the form of aerosols or fumigants.

The amount of the synergistic mixture to be used in plant protection agents can vary within wide limits. Among other things, it depends on the ratio of the components, on the type of preparation, on the method of application, on the intended control level and on the type of the pests to be controlled. /3

Depending on the type of preparation, the content of the synergistic mixture can measure between approximately 0.1 and 90 wt% of the agents that can be used in concentrations down to 0.001 wt%. Generally, however, application concentrations between approximately 0.025 and 10% in liquid or solid carrier materials lead to excellent results. For some purposes, higher application concentrations may be desirable.

In the synergist mixtures according to the present invention, the weight ratio between the components generally can measure approximately 25 parts by weight to 1 part by weight of the effective components and approximately 1-50 parts by weight of the ineffective components. Preferably, synergistic mixtures with a weight ratio of 1-10 parts of the effective carbamate to 5-50 parts of the ineffective compounds are used.

In repeated laboratory tests, after a metered application ( $4 \text{ mg/cm}^2$ ) in the form of aqueous emulsions up to concentrations of at least 0.25 vol%, the carbamic acid esters listed in Table 1 below were ineffective against

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House flies (*Musca domestica* L.) after continuous exposure for 24 h to spray coatings,  
granary weevils (*Sitophilus granarius* L.) after continuous exposure for 4 days to spray  
coatings.

Common stick insect (*Carausius morosus* Brunner) after an immersion treatment and after  
exposure for 5 days to treated forage crop plants,

Cockroaches (*Blatella germanica* L., *Periplaneta americana* L., *Leucophaea maderae* F.)  
after an immersion treatment or after exposure for 4 days to spray coatings,  
Asian gypsy moths (*Lymantria dispar* L.) after a metered treatment of the adult insects  
and after exposure of the larvae for 4 days to treated forage crop plants.

A comparison with the currently known insecticides that are fully effective at considerably lower concentrations under identical experimental conditions especially clearly underlines the inefficacy of the compounds tested, that hardly justifies their use in the practice of pest control from an economic standpoint.

TABLE I

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## Ineffective carbamic acid esters

Compound No.	Chemical name
1	3-Methyl-5-isopropylphenyl-N-cyclohexyl carbamate
2	Morpholine-N-carboxylic acid (3-methyl-5-isopropylphenyl) ester
3	Pyrrolidine-N-carboxylic acid (3-methyl-5-isopropylphenyl) ester
4	3,5-Dimethylphenyl-N,N-diisopropyl carbamate
5	3,5-Dimethylphenyl-N-(3-methylphenyl) carbamate
6	Piperidine-N-carboxylic acid (3,5-dimethylphenyl) ester
7	Morpholine-N-carboxylic acid benzyl ester
8	Morpholine-N-carboxylic acid allyl ester
9	Piperidine-N-carboxylic acid octyl ester
10	Dodecyl-N,N-diallyl carbamate
11	$\beta$ -(Butoxyethoxy)ethyl-N-(3-methylphenyl) carbamate
12	$\beta$ -(Butoxyethoxy)ethyl-N,N-diisopropyl carbamate
13	$\beta$ -(Butoxyethoxy)ethyl-N,N-diallyl carbamate
14	Ethyleneimine-N-carboxylic acid (3-methyl-5-isopropylphenyl) ester
15	Ethyleneimine-N-carboxylic acid dodecyl ester
16	3,5-Dimethylphenyl-N-( $\beta$ -chloroethyl) carbamate
17	Ethyleneimine-N-carboxylic acid $\beta$ -(butoxyethoxy)ethyl ester
18	Allyl-N-( $\beta$ -chloroethyl) carbamate
19	3-Methyl-6-isopropylcyclohexyl-N-methyl carbamate
20	2-Propenyl-4-methylphenyl-N-methyl carbamate

The compounds listed above were tested after mixing them with the carbamate known to be effective

## B. 1-naphthyl-N-methyl carbamate

at various ratios of the individual components. The synergistic effect of the mixtures according to the

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present invention is clearly demonstrated by the following examples. The degrees of efficacy listed in Tables 2 and 3 are average values obtained from at least two test series that had been carried out under identical conditions.

Example 1

To test the effect on common stick insects (*Carausius morosus* Brunner) after contact with the agent, fifteen freshly molted larvae IV each were immersed for three seconds in aqueous emulsions of each mixture according to the present invention, the excess liquid still adhering to the larvae was blotted off on filter paper, and the larvae were placed on spiderwort shoots that were used as forage crop plants in a wire gauze cage. In the daily efficacy tests, we distinguished between dead insects, severely injured insects, insects that react to a contact stimulus only with uncoordinated movements of the extremities, mildly injured insects and normally surviving insects. The test results obtained by means of ABBOT calculations are listed in Table 2.

TABLE 2

The effect of synergistic mixtures on *Carausius morosus* Brunner

(larvae IV) after immersion contact

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Compound (name or No.)	Active substance concentration in %	Percent efficacy after				
		1	2	3	4	5
B	0.02	7	7	10	13	15
	0.04	10	10	15	20	20
	0.1	20	33	47	73	85
	0.2	42	69	83	89	100
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Synergistic mixtures of						
B + 1	0.02 + 0.1	63	67	70	90	93
B + 2	0.02 + 0.1	83	93	100	—	—
B + 3	0.02 + 0.1	80	100	—	—	—
B + 4	0.02 + 0.1	83	100	—	—	—
B + 5	0.02 + 0.1	97	100	—	—	—
B + 6	0.02 + 0.1	83	100	—	—	—
B + 11	0.02 + 0.1	70	93	97	100	—
B + 12	0.02 + 0.1	77	90	100	—	—
B + 13	0.02 + 0.1	43	73	80	83	93
B + 14	0.02 + 0.1	60	77	77	83	83
B + 15	0.02 + 0.1	80	80	87	93	100
B + 16	0.02 + 0.1	97	100	—	—	—
B + 17	0.02 + 0.1	7	27	30	30	40
B + 18	0.02 + 0.1	53	67	77	77	83
B + 19	0.02 + 0.1	47	73	73	73	75
B + 20	0.02 + 0.1	67	100	—	—	—

Example 2

To test the effect of the substances on German cockroaches (*Blatella germanica* L.), ten male imagoes each that had been anesthetized with CO<sub>2</sub> were transferred into beaker glasses into that aqueous emulsions of the mixtures according to the present invention were poured, and immediately thereafter, the excess liquid adhering to the insects was blotted off on filter paper. During the experiment that lasted 3 days, the cockroaches were kept in gauze cages on a neutral filter substrate. The results of the efficacy

tests after 3 days in which we differentiated between dead, injured and normal experimental insects are summarized in Table 4 [sic; 3].

TABLE 3

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The effect of the synergistic mixtures on male imagoes of *Blatella germanica* L. after immersion contact

Compound (name or No.)	Active substance concentration in %	Percent efficacy after 3 days
B	0.02	50
	0.05	80
	0.1	100
Synergistic mixtures of		
B + 8	0.02 + 0.1	75
B + 7	0.02 + 0.1	80
B + 9	0.02 + 0.1	75
B + 10	0.02 + 0.1	100
B + 18	0.02 + 0.1	85

Claim

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1. An insecticide comprising a synergistic mixture of carbamates, characterized in that it contains one of the carbamates listed below that is insecticidally ineffective in a dose up to approximately 0.8 mg/dm<sup>2</sup>:

3-methyl-5-isopropylphenyl-N-cyclohexyl carbamate,  
morpholine-N-carboxylic acid (3-methyl-5-isopropylphenyl) ester,  
pyrrolidine-N-carboxylic acid (3-methyl-5-isopropylphenyl) ester,  
3,5-dimethylphenyl-N,N-diisopropyl carbamate,  
3,5-dimethylphenyl-N-(3-methylphenyl) carbamate,

piperidine-N-carboxylic acid (3,5-dimethylphenyl) ester,  
morpholine-N-carboxylic acid benzyl ester,  
morpholine-N-carboxylic acid allyl ester,  
piperidine-N-carboxylic acid octyl ester,  
dodecyl-N,N-diallyl carbamate,  
 $\beta$ -(butoxyethoxy)ethyl-N-(3-methylphenyl) carbamate,  
 $\beta$ -(butoxyethoxy)ethyl-N,N-diisopropyl carbamate,  
 $\beta$ -(butoxyethoxy)ethyl-N,N-diallyl carbamate,  
ethyleneimine-N-carboxylic acid (3-methyl-5-isopropylphenyl) ester,  
ethyleneimine-N-carboxylic acid dodecyl ester,  
3,5-dimethylphenyl-N-( $\beta$ -chloroethyl) carbamate  
ethyleneimine-N-carboxylic acid  $\beta$ -(butoxyethoxy)ethyl ester.  
allyl-N-( $\beta$ -chloroethyl) carbamate,  
3-methyl-6-isopropylcyclohexyl-N-methyl carbamate or  
2-propenyl-4-methylphenyl-N-methyl carbamate

in a mixture with the insecticide effective below this dose comprises

1-naphthyl-N-methyl carbamate